COPOLYMERIZATION OF VINYLSULFONIC ACID DERIVATIVES

BY
VIRGINIA CAROLINE MENIKHEIM
B.S., Butler University, 1941
M.S., University of Illinois, 1949

AN ABSTRACT OF A THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE UNIVERSITY OF
ILLINOIS, 1952

URBANA, ILLINOIS
1952

COPOLYMERIZATION OF VINYLSULFONIC ACID DERIVATIVES

BY
VIRGINIA CAROLINE MENIKHEIM
B.S., Butler University, 1941
M.S., University of Illinois, 1949

AN ABSTRACT OF A THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE UNIVERSITY OF
ILLINOIS, 1952

URBANA, ILLINOIS
1952

ACKNOWLEDGMENT

The author expresses her sincere gratitude for the assistance and counsel she has received from Dr. Carl S. Marvel who suggested and directed this investigation.

She is indebted also to Mr. W. K. Taft at the University of Akron for the general evaluation of the elastomers prepared.

This work was done under the sponsorship of the Synthetic Rubber Division, Reconstruction Finance Corporation, as a part of the Government Synthetic Rubber Program.

R. UNIV. BIBLIOTHEEK LEIDEN

INTRODUCTION

Since it has been observed that the properties of a polybutadiene polymer can be modified by the presence of highly polar functional groups, the copolymerization of vinyl compounds with butadiene has been under investigation for the purpose of developing elastomers which exhibit good flexibility at low temperatures as well as good tensile strength and stress-strain properties. Improvement in the oil-resistant properties of such copolymers is also desirable.

The excellent low-temperature properties of polybutadiene are not appreciably effected by the presence of the carboxylic esters,[1] but the nitrile group causes the freezing point of the polymer to rise considerably. On the other hand, the more polar nitrile group imparts good oil resistance to the elastomer while the carboxylic ester has little or no effect on the solubility of the butadiene polymer in hydrocarbons.

It was thought that the presence of a polar group such as the sulfonic ester group might increase the cohesion through hydrogen bonding and thereby improve the stress-strain properties of polybutadiene without appreciably increasing the freezing point. The purpose of this work was to introduce a sulfonyl group into a linear hydrocarbon polymer chain and to investigate the properties of the resultant copolymers. Since Kohler [2] has demonstrated that a carbon-carbon double bond α-β to the sulfonyl group undergoes addition reactions in a manner similar to a carbon-carbon double bond conjugate to the carbon-oxygen double bond of a carbonyl group, a study of the copolymerization of vinylsulfonic acid derivatives with butadiene was initiated to evaluate this method of incorporating a sulfonyl group into a hydrocarbon polymer chain.

DISCUSSION

Although some copolymerizations of vinylsulfonic acid derivatives with other vinyl compounds have been reported, information concerning the nature and composition of the resultant copolymers is lacking. No record of a copolymer of a vinylsulfonic acid derivative with butadiene was found.

Esters of vinylsulfonic acid were prepared in the following manner: A mole of sodium sulfite was caused to react with a mole of ethylene dibromide to give sodium 2-bromoethanesulfonate.[3] Ethylene dibromide must be present in large excess to prevent the formation of

the sodium ethane-1, 2-disulfonate. The sodium 2-bromoethanesulfonate, suspended in chloroform and treated with phosphorus pentachloride yielded 2-bromoethanesulfonyl chloride which when treated with an alcohol in the presence of a tertiary amine resulted in the corresponding ester [4] of vinylsulfonic acid. The tertiary amine was used to dehydrohalogenate the 2-bromoethanesulfonyl chloride as well as neutralize the halogen acids released during the reaction.

A satisfactory emulsion system has been developed in which the esters of vinylsulfonic acid copolymerize with butadiene at 0° C. to yield copolymers containing various amounts of the ester units depending on the monomer charge. As the ester content is increased, the product exhibits increased cohesion and becomes shorter in nature; however, the copolymers are elastic even when the ratio of the butadiene to ester units is two to one.

Copolymers of butadiene with ethyl, *n*-butyl and *n*-hexyl vinylsulfonates respectively have been prepared for evaluation. These copolymers contained essentially the same ratio of ester to butadiene units. The properties of these elastomers show that, like the carboxylic ester, the sulfonic ester group does not add oil resistance to the polymer.

The stress-strain properties of the *n*-butyl vinylsulfonate copolymer are good and essentially equal to those of the GR-S standard; however, when the ester chain is shortened or lengthened, these properties deteriorate.

The freezing point of the *n*-butyl vinylsulfonate copolymer is —67° C. which is slightly higher than that of polybutadiene (f.p. about —72° C.) but considerably lower than the freezing point of any of the copolymers of butadiene in practical use. The stress-strain properties of the *n*-butyl vinylsulfonate copolymer are better than those for any other polymers with the same freezing point. The low temperature data for the ethyl and *n-hexyl* copolymers are not available.

The hydrolysis of the butadiene-*n*-butyl vinylsulfonate copolymer yielded a new product which is still a rubber, but the polymer is shorter, more tough, less elastic and does not appear to be a practical elastomer.

Vinylsulfonic acid was prepared by the hydrolysis of ethane-1, 2-disulfonyl chloride.[2] When the electron withdrawing sulfonyl chloride groups are on adjacent carbons, the compound is relatively unstable and even water is sufficient to result in the removal of one of the

sulfonyl chloride groups as sulfur dioxide and hydrochloric acid. The second sulfonyl chloride group is hydrolyzed and the resultant product is the α,β-unsaturated alkenesulfonic acid. The ethane-1, 2-disulfonyl chloride was synthesized by causing phosphorus pentachloride to react with sodium ethane-1, 2-disulfonate which was prepared by adding ethylene dibromide to a large excess of sodium sulfite in a minimum of water. The direct copolymerization of vinylsulfonic acid or one of its salts with butadiene failed in aqueous emulsions.

The copolymer of *n*-butyl vinylsulfonate with isoprene appeared to be very similar to that obtained with butadiene. *n*-Butyl vinylsulfonate has been copolymerized with styrene in emulsion to yield a product which resembles polystyrene. All these copolymerizations indicate that the reactivity ratio of the esters of vinylsulfonic acid to the common vinyl monomers is low. Butadiene, isoprene, and styrene will enter the growing polymer chain at a much faster rate than the vinylsulfonic ester.

N-Methyl vinylsulfonanilide [5] was prepared by treating ethane-1, 2-disulfonyl chloride with N-methyl aniline. N, N′-Dimethyl 2-anilinoethanesulfonanilide was obtained also. Copolymers of N-methyl vinylsulfonanilide with butadiene were prepared, but analysis for sulfur indicated that the reactivity ratio of the sulfonanilide is even less than that of the esters of vinylsulfonic acid.

n-Butyl 2-phenylvinylsulfonate was prepared to determine the effect of the presence of the β-phenyl group on the copolymerization of vinylsulfonic acid derivatives. This ester was obtained by treating 2-phenylvinylsulfonyl chloride with butanol in the presence of pyridine. The acid chloride was prepared by adding phosphorus pentachloride to sodium 2-phenylvinylsulfonate which had been synthesized by sulfonating styrene with dioxane sulfotrioxide [6] and neutralizing the acid with sodium carbonate. No copolymer of butadiene with *n*-butyl 2-phenylvinylsulfonate or sodium 2-phenylvinylsulfonate was obtained from an acqueous emulsion.

BIBLIOGRAPHY

1. Office of Rubber Reserve, private communications.
2. Kohler, Am. Chem. J., **19**, 728 (1897).
3. Marvel and Sparberg, "Organic Synthesis," Col. Vol. II, John Wiley and Sons, Inc., New York, 1943, p. 558.
4. Whitmore and Landau, J. Am. Chem. Soc., **68**, 1797 (1946).
5. Clutterbuck and Cohen, J. Chem. Soc., **121**, 120 (1922).
6. Bordwell and Rondestvedt, J. Am. Chem. Soc., **70**, 2429 (1948).

VITA

The author was born in Washington, Pennsylvania, on August 15, 1919. She attended the public schools of Lawrence and Indianapolis, Indiana, and graduated from Broad Ripple High School in June of 1937. In the fall of 1937 she entered Butler University and in June of 1941 she received the degree of Bachelor of Science in Chemistry. She was employed as a chemist by the Evans Milling Company, Indianapolis, Indiana, from July 1941 to November 1941 and by The Shoe Polish Division of The Best Foods, Inc., Indianapolis, from November 1941 to May 1944. After serving in the Womens Army Corps from May 1944 to December 1945, she was employed as a chemist by the Air Materiel Command, Dayton, Ohio, until she entered the Graduate College of the University of Illinois in February of 1948. She completed the requirements for the degree of Master of Science in Chemistry in the summer of 1949 and has held a Research Assistantship from June 1950 to February 1952.